

## Description

# Motor Fuel Additive Composition

### BACKGROUND OF INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to an alcohol motor fuel additive composition for bulk fuel addition. More particularly, this invention relates to a motor fuel additive composition comprising: (a) a fuel conditioner component comprising (i) a polar oxygenated hydrocarbon compound, and (ii) an oxygenated compatibilizing agent; and (b) an alcohol for use in bulk production of motor fuels containing alcohol allowing lower levels of alcohol while improving performance and decreasing ORI.

[0003] Furthermore, this invention relates to a motor fuel additive composition comprising: (a) a detergent component selected from the group consisting of (i) a reaction product component which is the reaction product of a substituted hydrocarbon and an amino compound, and (ii) a succinic anhydride or succinic dibasic acid and (iii) a poly-

butylamine or polyisobutylamine; and (b) a fuel conditioner component comprising (i) a polar oxygenated hydrocarbon compound, and (ii) an oxygenated compatibilizing agent; and (c) an alcohol, for use in bulk production of motor fuels containing alcohol allowing lower levels of alcohol while improving performance and decreasing ORI.

[0004] 2. Description of the Related Art

[0005] In North America ethanol (C<sub>2</sub>H<sub>5</sub>OH) or ethyl alcohol is generally produced from agricultural feedstocks such as corn, wheat, barley, and sugar cane. It can also be produced from cellulose materials such as wood, wood waste, sawdust and forestry waste, or it can be derived chemically from ethylene or ethane.

[0006] Ethanol can be used directly as an alternate transportation fuel or as an Octane enhancing component in gasoline. Ethanol/Gasoline blends up to a maximum of 10 percent by volume ethanol in gasoline, also known as "Gasohol" or "E10" (10 denoting 10% ethanol and 90% gasoline), have been marketed in the United States for the last two decades. Gasohol is used in existing gasoline vehicles without making any changes to the engine or other vehicle components, and without violating manufacturer's warranties.

[0007] When ethanol is added to gasoline, it modifies the fuel properties and affects the exhaust and evaporative emissions from the vehicles. Some of the property changes also affect the vehicle performance. The important property changes include increase in vapor pressure and octane number of the blend compared to base gasoline, enrichment of the air fuel ratio, and dilution effect on the gasoline. On the volumetric basis ethanol contains only about 65% energy compared to gasoline which results in lowering the fuel economy by approximately 2 to 3 percent.

[0008] Blending ethanol to gasoline increases the octane value,  $(R+M)/2$  by 2 to 3 numbers depending upon the amount of ethanol used and composition of base gasoline. Although ethanol is less volatile than gasoline, when mixed with gasoline it depicts higher vapor pressure than the base gasoline, contributing to an increase in evaporative hydrocarbon emissions. In some engines, the increased volatility can cause vapor lock problems during hot weather conditions. Ethanol offers an alternative to MTBE as a higher octane, oxygenated blending component in gasoline. Finally, ethanol derived from biomass is a renewable fuel and offers overall reductions in greenhouse

gas emissions based on the rational that carbon dioxide produced from the combustion of fuel is recycled for growing the biomass.

- [0009] The ethanol/gasoline blend has a higher vapor pressure than plain gasoline. In a typical blend of 10 volume percent ethanol, the Reid Vapor Pressure (RVP) is about 1 psi higher. This can result in a number of vapor related problems, which are accentuated in hot weather and at higher altitudes. These problems include vapor lock and fuel pump cavitation, both of which result in engine stalling and difficulty in re-starting the engine until the fuel system cools down..
- [0010] Vehicles using ethanol/gasoline blends also experience reduced fuel economy. Typically, a 10% blend of ethanol will result in a 2 to 3 percent decrease in gas mileage.
- [0011] With the gradual phase out of MTBE in the United States ethanol is becoming the oxygenate of choice for blending in gasoline.
- [0012] In view of the foregoing, it would clearly be advantageous to employ an additive in ethanol containing motor fuel compositions which reduces deposits in engine fuel intake systems and also avoids the formation of deposits in engine combustion chambers, thereby reducing or at least

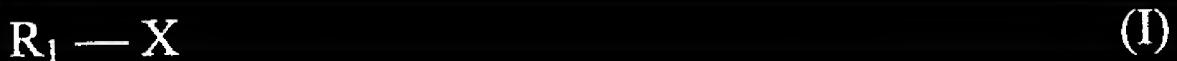
modifying the composition of deposits which tend to cause engine ORI.

## SUMMARY OF INVENTION

[0013] An ethanol containing motor fuel additive composition which reduces and modifies combustion chamber deposit formation for the purpose of reducing engine octane requirement increase and allows the use of lower levels of ethanol while retaining engine performance comprising a mixture of: (a) a fuel conditioner component comprising: (i) from about 2 to about 50 weight percent, based upon the total weight of the fuel conditioner component, of a polar oxygenated hydrocarbon having an average molecular weight in the range of about 200 to about 500, an acid number in the range of about 25 to about 175, and a saponification number in the range of about 30 to about 250, and (ii) from about 2 to about 50 weight percent, based upon the total weight of the fuel conditioner component, of an oxygenated compatibilizing agent preferably having a solubility parameter in the range of about 7.0 to about 14.0 and moderate to strong hydrogen capacity; and (b) ethanol.

[0014] Another object of the present invention is directed to an ethanol containing motor fuel additive composition that

reduces and modifies both fuel intake system and combustion chamber deposit formation for the purpose of reducing engine octane requirement increase and allows the use of lower levels of ethanol while retaining engine performance comprising a mixture of: (a) from about 5 to about 50 weight percent, based upon the total weight of components a and b, of a detergent component selected from the group consisting of (i) a reaction product of: (A) a substituted hydrocarbon of the formula

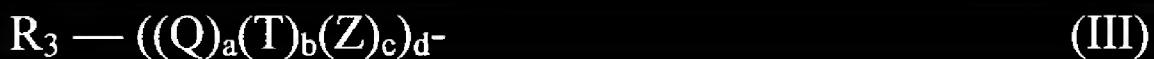


[0015] wherein  $R_1$  is a hydrocarbyl radical having a molecular weight in the range of about 150 to about 10,000, and X is selected from the group consisting of halogens, succinic anhydride and succinic dibasic acid, and (B) an amino compound of the formula



[0016] wherein Y is O or  $NR_5$ ,  $R_5$  being H or a hydrocarbyl radical having 1 – 30 carbon atoms; A is a straight chain or branched chain alkylene radical having 1 – 30 carbon atoms; m has a value in the range of 1 – 15; n has a value in the range of 0 – 6; and  $R_2$  is selected from the group consisting of H, a hydrocarbyl radical having a molecular

weight in the range of about 15 to about 10,000, and a homopolymeric or heteropolymeric polyoxyalkylene radical of the formula



[0017] wherein  $R_3$  is H or a hydrocarbyl radical having 1 – 30 carbon atoms, Q, T, and Z are polyoxyalkylene moieties having 1 – 6 carbon atoms, a, b and c each have values ranging from 0 – 30, and d has a value in the range of 1 – 50, and (ii) a polybutylamine or polyisobutylamine of the formula



[0018] where  $R_{11}$  is a polybutyl or polyisobutyl radical derived from isobutene and up to 20% by weight of n-butene and  $R_{12}$  and  $R_{13}$  are identical or different and are each hydrogen, an aliphatic or aromatic hydrocarbon, a primary or secondary, aromatic or aliphatic aminoalkylene radical or polyaminoalkylene radical, a polyoxyalkylene radical or a heteroaryl or heterocyclyl radical, or, together with the nitrogen atom to which they are bonded, form a ring in which further hetero atoms may be present; and (b) a fuel

conditioner component comprising: (i) from about 2 to about 50 weight percent, based upon the total weight of components a and b, of a polar oxygenated hydrocarbon having an average molecular weight in the range of about 200 to about 500, an acid number in the range of about 25 to about 175, and a saponification number in the range of about 30 to about 250, and (ii) from about 2 to about 50 weight percent, based upon the total weight of components a and b, of an oxygenated compatibilizing agent preferably having a solubility parameter in the range of about 7.0 to about 14.0 and moderate to strong hydrogen capacity; and (c) ethanol.

- [0019] The fuel conditioner component may additionally comprise a hydrophilic separant such as a glycol monoether. The additive composition may additionally comprise a carrier oil or fluidizer.
- [0020] This invention is also directed to an ethanol containing motor fuel containing the present invention which may be added with the ethanol and any other additives or added after the addition of the ethanol and any other additives.

#### **DETAILED DESCRIPTION**

- [0021] This invention is in one aspect directed to an ethanol containing motor fuel additive comprising: (a) a detergent

component which is selected from the group consisting of (i) the reaction product of a substituted hydrocarbon and an amino compound, (ii) a polybutylamine or polyisobutylamine; (b) a fuel conditioner component comprising a polar oxygenated hydrocarbon compound and an oxygenated compatibilizing agent; and (c) ethanol.

[0022] Another aspect of the present invention is directed to an ethanol containing motor fuel additive comprising (a) a fuel conditioner component comprising a polar oxygenated hydrocarbon compound and an oxygenated compatibilizing agent; and (b) ethanol.

[0023] If the reaction product detergent component is employed, the substituted hydrocarbon reactant used to prepare the reaction product is of the formula

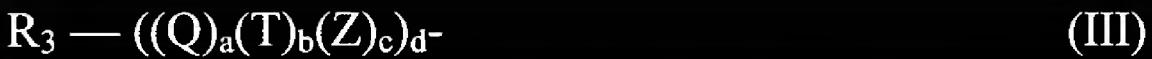


[0024] wherein  $R_1$  is a hydrocarbyl radical having a molecular weight in the range of about 150 to about 10,000, preferably a polyalkylene radical having a molecular weight in the range of about 400 to about 5000, most preferably a polyalkylene radical having a molecular weight in the range of about 600 to about 1500, and X is selected from the group consisting of halogens, preferably chlorine, succinic anhydride and succinic dibasic acid. in one pre-

ferred embodiment,  $R_1-X$  is a polyisobutetyl succinic anhydride. In another preferred embodiment,  $R_1-X$  is a chloropolyisobutylene. The amino compound reactant used to prepare the reaction product is of the formula



[0025] wherein Y is O or  $NR_5$ ,  $R_5$  being H or a hydrocarbyl radical having 1 – 30 carbon atoms, preferably 1 – 22 carbon atoms; A is a straight chain or branched chain alkylene radical having 1 – 30, preferably 1 – 15 carbon atoms; m has a value in the range of 1 – 15, preferably 1 – 12; n has a value in the range of 0 – 6, preferably 0 – 5; and  $R_2$  is selected from the group consisting of H, a hydrocarbyl radical having a molecular weight in the range of about 15 to about 10,000, preferably 15 to about 2000, and a homopolymeric or heteropolymeric polyoxyalkylene radical of the formula



[0026] wherein  $R_3$  is H or a hydrocarbyl radical having 1 – 30, preferably 1 – 22 carbon atoms, Q, T, and Z are polyoxyalkylene moieties having 1 – 6 carbon atoms, a, b, and c each have values ranging from 0 – 30, and d has a value in the range of 1 – 50, preferably 1 – 25.

[0027] Various preferred embodiments of the amino compound reactant of formula (II) are given in Table 1 below:

[0028] Table 1

[0029] 1.  $A=CH_2$ ,  $m=2$ ,  $n=3$ ,  $Y=NR_5$ ,  $R_5=H$ ,  $R_2=H$ , yields an amino compound reactant of the formula:



[0030] 2.  $A=CH_2$ ,  $m=3$ ,  $n=1$ ,  $Y=NR_5$ ,  $R_5=H$ ,  $R_2=$ oleyl radical, yields an amino compound reactant of the formula:



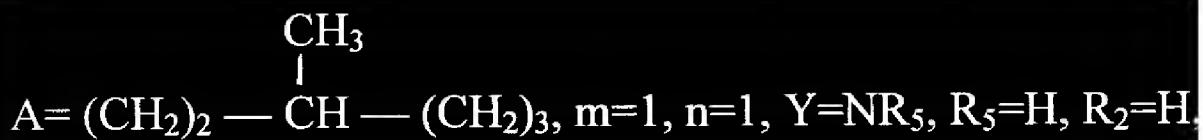
[0031] 3.  $A=CH_2$ ,  $m=6$ ,  $n=1$ ,  $Y=NR_5$ ,  $R_5=H$ ,  $R_2=H$ , yields an amino compound reactant of the formula:



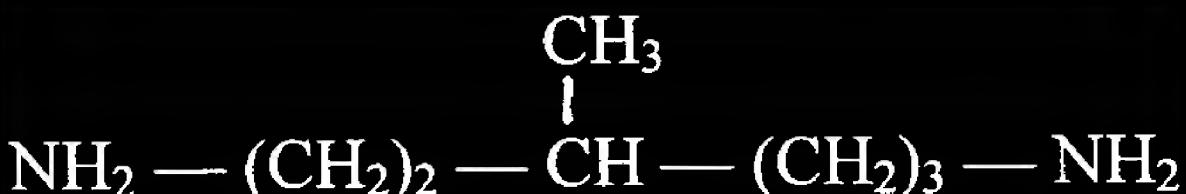
[0032] 4.  $A=CH_2$ ,  $m=12$ ,  $n=1$ ,  $Y=NR_5$ ,  $R_5=H$ ,  $R_2=H$ , yields an amino compound reactant of the formula:



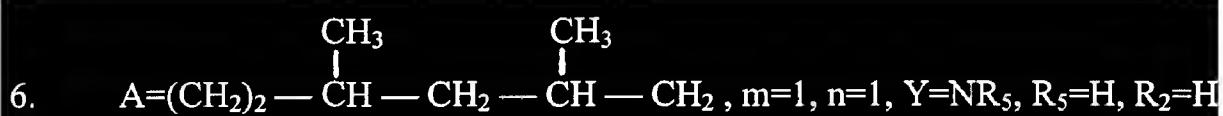
[0033] 5.



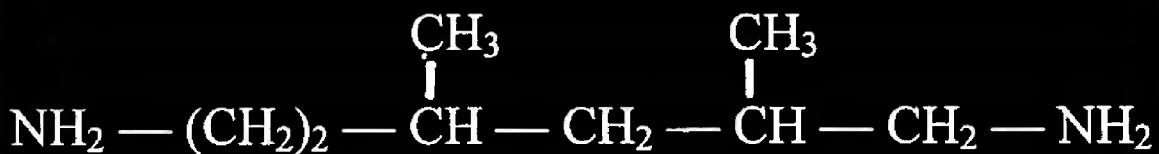
[0034] yields an amino compound reactant of the formula:



[0035] 6.



[0036] yields an amino compound reactant of the formula:



[0037] In another preferred embodiment,  $R_2$  is the above-described homopolymeric or heteropolymeric polyoxyalkylene radical of formula (III). As used in this description and in the appended claims, the terms homopolymeric and heteropolymeric refer to polyoxyalkylene compounds, which in the case of homopolymeric compounds contain one recurring polyoxyalkylene moiety, and in the case of heteropolymeric compounds contain more than one re-

curing polyoxyalkylene moiety, typically having 1–6 carbon atoms, such as ethylene oxide (EO), propylene oxide (PO) or butylene oxide (BO). Thus, for example, in one embodiment  $R_2$  may be a homopolymeric polyoxyalkylene radical of the formula



[0038] wherein in formula (III),  $a = 1$ ,  $b = 0$ ,  $c = 0$ ,  $Q =$  ethylene oxide, and  $R_3$  and  $d$  are as previously defined. In another embodiment,  $R_2$  may be a heteropolymeric polyoxyalkylene radical of the formula



[0039] wherein, in formula III,  $Q =$  ethylene oxide,  $T =$  propylene oxide,  $Z =$  butylene oxide, and  $a$ ,  $b$ ,  $c$ ,  $d$  and  $R_3$  are as previously described.

[0040] In yet another preferred embodiment, the above-described amino compound reactant is selected from the group consisting of polyethylene polyamines, polypropylene polyamines and mixtures thereof. In yet another preferred embodiment, such polyamines are monoalkylated.

[0041] The reaction product component is preferably prepared by reacting the substituted hydrocarbon  $R_1-X$  to the amino compound in a mole ratio in the range of 0.2:1 – 20:1, more preferably in the range of 0.5:1 – 10:1. The reaction product component may be prepared under reaction conditions (including e.g. reaction times, temperatures, and reagent proportions) as are well known by those skilled in the art for preparing such amino compound–substituted hydrocarbon reaction products. The method for preparing such reaction products is described, for example, in U.S. Pat. No. 3,172,892 (LeSeur et al.), U.S. Pat. No. 3,438,757 (Honnen et al.), and U.S. Pat. No. 3,443,918 (Kautsky et al.), all of which are incorporated herein by reference.

[0042] The detergent compound may also be a polybutylamine or polyisobutylamine of the formula (IV)



[0043] where  $R_{11}$  is a polybutyl- or polyisobutyl radical derived from isobutene and up to 20% by weight of n-butene, and  $R_{12}$  and  $R_{13}$  are identical or different and are each hydrogen, an aliphatic or aromatic hydrocarbon, a primary or

secondary, aromatic or aliphatic aminoalkylene radical or polyaminoalkylene radical, a polyoxyalkylene radical or a heteroaryl or heterocyclyl radical, or, together with the nitrogen atom to which they are bonded, form a ring in which further hetero atoms may be present.

[0044] Compounds of the general formula (IV) and the method of preparation thereof are disclosed, for example, in U.S. Pat. No. 4,832,702 (Kummer et al.), incorporated herein by reference. Compounds of the general formula (IV) are preferably prepared in accordance with the method disclosed in U.S. Pat. No. 4,832,702, wherein an appropriate polybutene or polyisobutene is hydroformylated with a rhodium or cobalt catalyst in the presence of CO and H<sub>2</sub> at from about 80–200°C and CO/H<sub>2</sub> pressures of up to 600 bar, and the oxo product thereby formed is then subjected to a Mannich reaction or amination under hydrogenating conditions, wherein the amination reaction is advantageously carried out at 80 – 200°C and under pressures up to 600 bar, preferably 80 – 300 bar.

[0045] The fuel conditioner component employed in admixture with the detergent component to produce the additive of this invention may preferably be the fuel conditioner previously disclosed in U.S. Pat. No. 4,753,661 (Nelson et al.),

incorporated herein by reference. This fuel conditioner comprises a polar oxygenated hydrocarbon compound and an oxygenated compatibilizing agent.

[0046] The polar oxygenated hydrocarbon portion of the fuel conditioner signifies various organic mixtures arising from the controlled oxidation of petroleum liquids with air. Often these air oxidations of liquid distillates are carried out at a temperature of from about 100°C to about 150°C with an organo-metallic catalyst, such as esters of manganese, copper, iron, cobalt, nickel or tin, or organic catalysts, such as tertiary butyl peroxide. The result is a melange of polar oxygenated compounds which may be divided into at least three categories: volatile, saponifiable and non-saponifiable.

[0047] The polar oxygenated compounds preferable for use in the present invention may be characterized in at least three ways, by molecular weight, acid number, and saponification number. It is to be appreciated by those skilled in the art that the terms "molecular weight" and "average molecular weight" are synonymous and are herein used interchangeably. It is to be further appreciated that there are several methods of determining the average molecular weight of an organic material and that

different methods will produce different results for the same material. Chemically these oxidation products are mixtures of acids, hydroxy acids, lactones, esters, ketones, alcohols, anhydrides, and other oxygenated organic compounds. Those suitable for the present invention are compounds and mixtures with an average molecular weight between about 200 and about 500, with an acid number between about 25 and about 175 (ASTM-D-974), and a saponification number from about 30 to about 250 (ASTM-D-974-52). Preferably the polar oxygenated compounds of the present invention have an acid number from about 50 to about 100 and a saponification number from about 75 to about 200.

[0048] Suitable compatibilizing agents for use in the fuel conditioner component of the instant invention are organic compounds of moderate solubility parameter and moderate to strong hydrogen-bonding capacity. Solubility parameters,  $\delta$ , based on cohesive energy density are a fundamental descriptor of an organic solvent giving a measure of its polarity. Simple aliphatic molecules of low polarity have a low  $\delta$  of about 7.3; highly polar water has a high  $\delta$  of 23.4. Solubility parameters, however, are just a first approximation to the polarity of an organic solvent.

Also important to generalized polarity, and hence solvent power, are dipole moment and hydrogen-bonding capacity. Symmetrical carbon tetrachloride and some aromatics with low gross dipole moment and poor hydrogen-bonding capacity have a solubility parameter of about 8.5. In contrast, methyl propyl ketone has almost the same solubility parameter, 8.7, but quite strong hydrogen-bonding capacity and a definite dipole moment. Thus, no one figure of merit alone describes the "polarity" of an organic solvent.

- [0049] For the practice of the present invention a compatibilizing agent preferably having a solubility parameter from about 7.0 to about 14.0 and moderate to strong hydrogen-bonding capacity. Suitable classes of organic solvents are alcohols, ketones, esters, and ethers.
- [0050] The fuel conditioner component of this invention may additionally include a hydrophilic separant which decreases the amount of water in the hydrocarbon fuel, thus improving combustion. Suitable separants for practicing the current invention are ethers of glycols or polyglycols, especially monoethers. Monoethers are preferred over diethers in the practice of the present invention.
- [0051] Examples of such compounds which may be used are the

monoethers of ethylene glycol, propylene glycol, trimethylene glycol, alphabutylene glycol, 1,3- butanediol, beta-butylene glycol, isobutylene glycol, tetramethylene glycol, hexylene glycol, diethylene glycol, dipropylene glycol, tripropylene glycol, triethylene glycol, tetraethylene glycol, 1,5- pentanediol, 2-methyl-2-ethyl-1,3-propanediol, 2- ethyl-1,3-hexanediol. Some monoethers include ethylene glycol monophenyl ether, ethylene glycol monomethylether, ethylene glycol monoethyl ether, ethylene glycol mono-(n-butyl) ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether, diethylene glycol mono-(n-butyl) ether, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, diethylene glycol monocyclohexylether, ethylene glycol monobenzyl ether, triethylene glycol monophenethyl ether, butylene glycol mono-(p-(n-butoxy) phenyl) ether, trimethylene glycol mono(alkylphenyl) ether, tripropylene glycol monomethyl ether, ethylene glycol mono-isopropyl ether, ethylene glycol monoisobutyl ether, ethylene glycol monohexyl ether, triethylene glycol monobutyl ether, triethylene glycol monomethyl ether, triethylene glycol monoethyl ether, 1-butoxyethoxy-2- propanol, monophenyl ether of

polypropylene glycol having an average molecular weight of about 975 to 1075, and monophenyl ether of polypropylene glycol wherein the polyglycol has a average molecular weight of about 400 to 450, monophenyl ether of polypropylene glycol wherein the polypropylene glycol has an average molecular weight of about 975 to 1075.

Such compounds are sold commercially under trade names such as Butyl CELLOSOLVE, Ethyl CELLOSOLVE, Hexyl CELLOSOLVE, Methyl CARBITOL, Butyl CARBITOL, DOWANOL Glycol ethers, and the like.

[0052] The composition of this invention may additionally comprise a suitable amount of a carrier oil or fluidizer selected from the group consisting of petroleum-based oils, mineral oils, polypropylene compounds having a molecular weight in the range of about 500 to about 3000, polyisobutylene compounds having a molecular weight in the range of about 500 to about 3000, polyoxyalkylene compounds having a molecular weight in the range of about 500 to about 3000, and polybutyl and polyisobutyl alcohols containing polybutyl or polyisobutyl radicals derived from polyisobutene and up to 20% by weight of n-butene, corresponding carboxylates of the polybutyl or polyisobutyl alcohol, and mixtures thereof. Petroleum based

oils which may be employed include top cylinder oils as well as both natural and synthetic naphthenic and paraffinic base stock oils of relatively high viscosity, including so-called Solvent Neutral Oils (SNO) such as SNO-500 and SNO-600. Mineral oils which may be employed include so-called "light" mineral oils, i.e. those petroleum, aliphatic or alicyclic fractions having a viscosity less than about 10,000 SUS at 250°C. A mixture of hydrocarbon fractions may also be employed in place of a base stock. The above-described polybutyl and polyisobutyl alcohols include those disclosed in U.S. Pat. No. 4,859,210 (Franz et al.), incorporated herein by reference. As used in this description and in the appended claims, the terms "carrier oil" and "fluidizer" are interchangeable, as will be readily understood by those skilled in the art.

[0053] Given the presence of the many constituents described above, a wide variety of proportions are suitable for the additive composition of this invention. Below a "Useful Range" and a "Preferred Range" are given in weight percent, based upon the total weight of the additive composition:

Table 2

Component	Useful Range	Preferred Range
Detergent Component	5 - 50	10 - 40
Polar Oxygenated Compound	2 - 50	10 - 40
Compatibilizing Agent	2 - 50	5 - 25
Hydrophilic Separant	0 - 40	0 - 30
Carrier Oil	0 - 40	0 - 30
Ethanol	balance of the additive package is ethanol	

[0054] The additive composition of this invention may be employed in a wide variety of hydrocarbon or modified hydrocarbon (e.g. alcohol-containing) fuels for a variety of engines. Preferred motor fuel compositions for use with the additive composition of this invention are those intended for use in spark ignition internal combustion engines. Such motor fuel compositions, comprise a fuel component generally referred to as gasoline base stocks, preferably comprise a mixture of hydrocarbons boiling in the gasoline boiling range, preferably from about 90–450°F. This base fuel may consist of straight chains, branch chains, paraffins, cycloparaffins, olefins, aromatic hydrocarbons, and mixtures thereof. The base fuel may be derived from, among others, straight run naphtha, polymer gasoline, natural gasoline, or from catalytically cracked or thermally cracked hydrocarbons and catalytically reformed stock. The composition and octane level of

the base fuel are not critical and any conventional leaded motor base fuel may be employed in the practice of this invention. In addition, the motor fuel composition may additionally comprise other additives typically employed in motor fuels, such as anti-icing additives, upper cylinder lubricating oils, carburetor detergents, anti-corrosion additives, de-emulsifying agents, odor suppressors, and the like.

- [0055] Throughout the specification, examples and claims the following definitions are used.
- [0056] Combustion Chamber Deposits (CCD) means deposits formed in the combustion chamber of an engine, due to the deposition of carbonaceous deposits of unburned fuel components and deposits from other additives present in the fuel.
- [0057] Octane Requirement Increase (ORI) means the increase in octane requirement that results from the build up of combustion chamber deposits. ORI begins to build up as soon as a new engine is started for the first time as CCDs begin to form in the combustion chamber of the engine. ORI reaches equilibrium between 10,000 to 15,000 miles in the life of a new engine. The octane requirement increase is typically 5-8 octane numbers by the time equilibrium is

reached.

- [0058] Octane Number Required (ONR) means the octane level required to provide knock-free operations in a given engine.
- [0059] Octane Enhancer means components that are added to gasoline to increase octane and to reduce engine knock, such as for example, ethanol.
- [0060] The present invention fuel conditioner contains only carbon, hydrogen, and oxygen and has been approved by the United States EPA as substantially similar to gasoline, thus allowing for bulk treatment of unleaded gasoline. The present invention, less the alcohol content, is used in very low treatment rates ranging from about 100 to 1000 parts per million (ppm). Testing has shown that the present invention accelerates combustion, releasing the energy earlier in the combustion process, which results in improved power, more complete combustion, and cooler exhaust gas temperatures. In addition the present invention has been shown to reduce ORI and ONR by from about 50% to about 80% equivalent to about 2 to 5 octane numbers in gasoline engines. The results are improved vehicle performance, reduced ONR, improved fuel economy, cleaner combustion chambers with lower maintenance costs, as

well as lower CO and HC emissions.